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A STUDY OF CONTACT POTENTIALS AND PHOTO-ELECTRIC PROPERTIES OF METALS IN VACUO: AND THE MUTUAL RELATION BETWEEN THESE PHENOMENA

A DISSERTATION
SUBMITTED TO THE FACULTY OF THE OGDEN GRADUATE SCHOOL OF SCIENCE IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
DEPARTMENT OF PHYSICS

BY
ALBERT EDWARD HENNINGS

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A STUDY OF CONTACT POTENTIALS AND PHOTO-ELECTRIC PROPERTIES OF METALS IN VACUO: AND THE MUTUAL RELATION BETWEEN THESE PHENOMENA.

BY ALBERT E. HENNINGS.

THREE years ago Professor Millikan suggested as a promising subject for research, the careful study of the contact potential differences between metals in vacuo under conditions which would eliminate the effects of surface films. He considered it imperative that such a study be undertaken both because of the light which it ought to throw on the true nature of contact potentials and because his own photo-electric studies had produced evidence that the positive potentials acquired by metals under the influence of ultra-violet light were very probably related in some definite, but not yet fully understood way, to the contact potential differences between the metals. After carrying on preliminary experiments for a year or more with different types of tubes, the writer decided upon the experimental arrangement and designed the apparatus which have been used in the work herein reported.

The plan in brief was to test, simultaneously and in vacuo, the contact potentials and photo-electric properties of eight of the ordinary metals not only under conditions which have usually obtained in the study of either of these phenomena, viz., with surfaces prepared in air and subsequently surrounded by a vacuum, but also with surfaces mechanically prepared in a vacuum which was the best obtainable and which was maintained throughout all operations, and finally to observe the time changes in contact potential differences and photosensitiveness of photo-electrically or mechanically treated surfaces.

So far as I am aware no experiments have been made heretofore on the contact potential differences between metal surfaces freed from gas or oxide films. The chemical theory of contact potentials makes the whole effect depend essentially upon the existence of such films. Hence the significance of experiments of this kind upon the theory of contact potentials. Photo-electric experiments on clean surfaces in vacuo, however, have already been made and described by Pohl and Pringsheim,[1]

[1] Verh. d. Deutch Phys. Ges., 13, 474, 1911; 14, 46, 506, 546, 1912.

and Hughes,[1] using freshly distilled surfaces and by Herrmann,[2] Richardson and Compton,[3] and Page,[4] using mechanically cleaned surfaces.

THE RESULTS.

The facts which may be considered as having been definitely established by the present investigation are the following:

1. The contact potentials of the metals are not noticeably changed by differences in pressure ranging from atmospheric pressure to that of the best vacuum obtained.

2. All the metals are rendered more electro-positive when polished in vacuo and gradually become more electro-negative just as do freshly polished surfaces in air.

3. Prolonged illumination with ultra-violet light greatly modifies the contact potentials of film coated surfaces, and whatever the direction or magnitude of the change may be each metal exhibits a tendency to recover its original potential when the action of the light has ceased. With newly prepared surfaces these changes are negligible or inappreciable.

4. On the photo-electric side the results as a whole confirm the point of view adopted by Richardson and Compton in regard to the relation between photo- and contact potentials.

5. The photo-sensitiveness of all the metals is very largely increased when the surface films, which in general always exist even in the best vacuum unless the metals have been subjected to special treatment as described below, are removed.

6. Although the order of the metals when arranged according to their photosensitiveness in vacuo is usually not at all that of the Volta contact series, the order assumed by freshly cleaned metals approaches very closely that of this series.

DESCRIPTION OF APPARATUS AND OUTLINE OF EXPERIMENTAL PROCEDURE.

The apparatus designed for this study is enclosed in a glass bulb about 13 cm. in diameter with five projecting arms—four being in the horizontal plane and the fifth occupying a vertical position—the axes of all meeting at the center of the bulb. Fig. 1 represents a horizontal section in the plane of the intersecting axes of the two pairs of projecting arms and Fig. 2 represents a vertical section in the plane including the vertical

[1] Roy. Soc., Phil. Trans., 212, pp. 205–226.
[2] Verh. d. Deutch Phys. Ges., 14, 557, 1912.
[3] Phil. Mag., 24, pp. 575–594.
[4] Amer. Jour. Sci., 36, 501, 1913.

axis and that of one of the pairs of projecting arms. The horizontal arms are 42 to 45 mm. in diameter.

Eight metals, magnesium, aluminum, zinc, tin, iron, brass, copper, silver, in the form of disks 2 cm. in diameter are mounted upon an amber

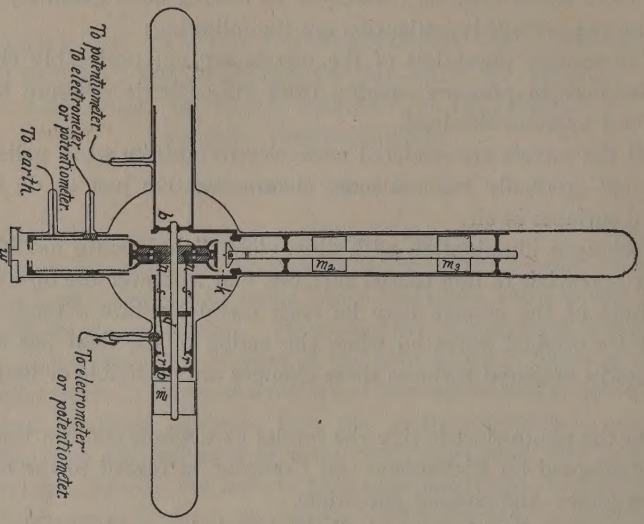

Fig. 1.

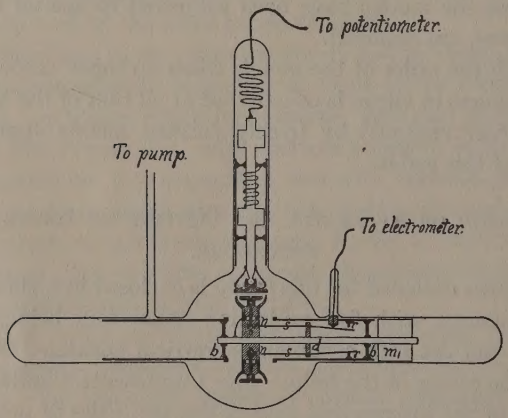

Fig. 2.

hub 38 mm. in diameter with the planes of their faces parallel to the axis of the wheel so formed. To one end of the rod passing through the hub and supporting it by means of suitable bearings *b*, *b*, in brass tubes

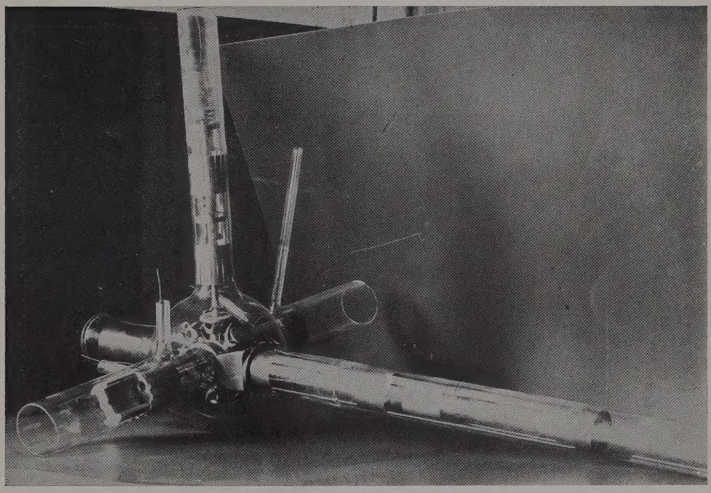

Fig. 2*a*.

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joined rigidly together and fitted firmly in the projecting arms of the bulb is attached a double anchor-shaped piece of iron, m_1. By means of an external electro-magnet the wheel may be rotated and if necessary moved a short distance along the axis, making it possible to adjust very accurately the position of any of the eight metal disks.

The longest of the projecting arms is fitted with a brass tube which is attached to, and holds rigidly together, the brass tubes which support the axle of the wheel. This tube serves also to give support to the bearings for a rod carrying at its inner end a well-tempered wedge-shaped steel tool, k, 2 cm. wide, and at two other points the iron armatures, m_2 and m_3. The latter by means of a second external electro-magnet may be rotated and moved along the axis. The knife-edge is thus made to rotate and simultaneously to press against the surface of one of the metal disks brought into juxtaposition. By this device all of the eight metal surfaces were effectively scraped off in vacuo. With the softer metals precaution had to be taken so as not to cut away too much. To insure the successful operation of this device the knife carries at its middle point a thin conical projection which fits into a hole in the center of the disk. In order that the knife may always bear upon the whole surface the rod is jointed very near its inner end.

The shortest of the projecting arms carries a brass cylinder with an inner concentric one of a double layer of fine meshed wire gauze. Both cylinders were blackened by oxidation and are insulated from each other with amber. The further end of the double cylinder so formed is closed save for a central circular opening 11 mm. in diameter through which ultra-violet light may be directed upon one of the metal disks when brought into such a position as to practically close the double cylinder at the inner end which is open and as near the wheel as possible without interfering with its motion. The ultra-violet light is admitted through the thin quartz window, w, which closes a circular opening 9 mm. in diameter in a heavy glass plate. Both the quartz and glass plates are sealed on with de Khotinsky cement. The outer brass cylinder was earthed in this work and the inner one of gauze was used as the receiving electrode for the measurements of the photo-currents.

The metal under investigation is insulated from all the rest by means of the commutator arrangement now to be described. Leading from the brass nuts, n, into which the rods attached to the metal disks are screwed, are the heavy steel wires, s, one for each of the disks. These wires are held apart by the amber disk, d, which is fixed upon the axle of the wheel, and which causes the wires to press against an immovable ring, r, inserted inside the brass supporting tube. When the wheel

rotates each wire slides over and remains in contact with the inner surface of this ring except at two points in a complete revolution, one when the disk to which the wire is attached is in position for ultra-violet light illumination and the other when it is in position for the measurement of the contact potential. (This latter position will be indicated and the manner in which the measurement is made will be described presently.) At these two points the steel wire is forced to break contact with the ring by means of a curved piece of brass which is insulated by means of amber. The platinum wire, *l*, leading to the brass is then in communication with the now insulated disk. To insure the best possible contact the curved piece of brass and the brass ring are faced with platinum and each of the wires at the two points where contact is made is likewise covered with platinum. There is a second amber disk (omitted from the diagram to avoid confusion) placed near the end of the wires, which is slotted radially and which serves to prevent each wire from being carried around by the friction between it and the surface with which it is making contact. The plate under illumination may be charged to various potentials and the distribution of velocity curve determined by observing the rate with which the wire gauze cylinder used as receiving electrode charges up. This procedure was the one adopted for the major portion of the photo-electric data recorded in this paper. Measurements of the positive potentials acquired by the insulated plate when exposed to ultra-violet light were also made by putting the plate in communication with the electrometer and applying the accelerating or retarding potentials to the wire gauze cylinder.

The vertical arm supports by means of an inserted brass frame a spool-shaped piece of iron which carries at its lower extremity a brass plate $3\frac{1}{2}$ cm. in diameter. A solenoid outside the tube is used to raise or to lower the brass plate, which with each of the metal surfaces in turn constitutes the condenser system employed in determining the contact potentials. The metal disk which is to be examined when brought into position directly beneath the vertical tube is insulated by the commutator device already described. The two surfaces are brought near together by lowering the brass plate upon the three projecting arms which surround, but are insulated from, the disk. The plane of the points of these three arms was made as nearly parallel as possible to that of the disk and about .12 mm. (before the surfaces were scraped) above it. It is not essential that the two planes be absolutely parallel if for each combination the relative position of each of the surfaces when near together is always exactly the same. The brass plate must therefore never fail to rest upon all three points when lowered. This condition

is met by having the brass plate upon a ball and socket joint. Between the rod above the joint and the back of the plate are attached also three brass springs, the purpose of which is to make certain that the movable plate is kept horizontal when it is being moved away from the disk beneath. A portion of the weight of the iron spool is born by a spiral spring attached between it and the supporting frame in order that the solenoid need not be inconveniently large.

Theoretically the simplest way to determine the contact potential between the brass plate and the metal disk underneath would be to place such a potential upon the brass plate and all the metal parts of the apparatus except the metal disk under observation which is in communication with the electrometer and which is first grounded and then insulated, that no deflection of the electrometer needle is observed upon raising the brass plate, but practically this procedure is not sufficiently expeditious. It proved far more satisfactory to apply to the movable plate and the framework some convenient positive potential and then with a reversing key, the same negative potential, observing in each case the electrometer deflection when the upper plate was raised. Proceeding in this manner the contact potential difference is determined by the relationship

$$E = PD \frac{d_1 + d_2}{d_1 - d_2},$$

where

E represents the contact potential difference.

PD represents the potential positively or negatively applied to movable plate.

d_1 represents deflection when $+ PD$ is applied.

d_2 represents deflection when $- PD$ is applied.

The deflections must of course be taken with their sign. The mean of these two deflections is the deflection observed with no charge applied to the movable plate. The several metals are thus compared with the brass plate. The contact potential difference between any pair may be taken as the difference between the contact potential differences of each of the pair with brass.

Preliminary Measurements of the Contact Potentials.

When the parts of the apparatus had been assembled in the bulb, the contact potentials were measured before sealing up the tubes through which the various parts had been introduced. The numbers in the first column in Table I. represent the values in volts observed for each of the metals when compared with the movable brass plate. The second

column gives a series of values obtained with the closed tube after remaining for several days filled with ordinary air at atmospheric pressure. The third column gives the value for dry air, *i. e.*, the air had been pumped out and dry air introduced, the process being repeated a number of times and the apparatus then left to stand several days after sealing up with drying tubes of phosphorus pentoxide. The bulb was then again exhausted and left so for three days, when it was again filled and exhausted. The results given in columns III., IV., V. and VI. exhibit nothing which can be attributed to changes in pressure. The seventh column gives the values obtained with a very low vacuum which had been reached after several days pumping with a Töpler pump and the use of cocoanut charcoal. The remaining columns give the values obtained in succeeding intervals during all of which time the best possible vacuum was maintained. Mercury vapor was prevented from entering the bulb by means of gold foil which filled the glass tube leading to the pump for 40 cm. of its length.

TABLE I.

Metal.	I. Mar. 17, Open Tube Atmos. Pressure.	II. Apr. 25, Sealed Tube Atmos. Pressure.	III. May 16, Atmos. Pressure.	IV. May 18, Vacuum.	V. May 19, Vacuum.	VI. May 20, Atmos. Pressure.	VII. June 3, Vacuum.	VIII. July 1, Vacuum.	IX. July 17, Vacuum.	X. July 24, Vacuum.
Silver	−.16	−.11	−.076	−.076	−.080	−.081	−.073	−.081	−.079	−.084
Tin	+.29	+.31	+.296	+.291	+.285	+.281	+.260	+.248	+.230	+.232
Magnesium	+.98	+.95	+.918	+.911	+.904	+.894	+.890	+.87	+.88	+.86
Zinc	+.35	+.32	+.300	+.295	+.296	+.289	+.285	+.267	+.254	+.248
Aluminum	+.50	+.45	+.428	+.419	+.417	+.410	+.422	+.394	+ 382	+.373
Iron	−.017	+.02	+.031	+.031	+.026	+.027	+.030	+.027	+.038	+.030
Copper	−.08	−.06	−.054	−.062	−.048	−.057	−.059	−.067	−.067	−.075
Brass	−.03	−.02	−.017	−.015	−.022	−.026	−.028	−.034	−.032	−.032

A survey of all the results in Table I. shows that the contact potentials must be independent of pressure. None of the changes are abrupt, indicating that they are all due to the mere ageing with time. The metals on the whole have become more electro-negative. This does not appear to be true in all cases, but the apparent discrepancy lies in the fact that the brass plate with which these metals have been compared is also subject to changes.

THE EFFECT OF ILLUMINATION WITH ULTRA-VIOLET LIGHT UPON THE CONTACT POTENTIALS OF FILM COATED SURFACES.

The illumination of the surfaces of the metals with ultra-violet light was effected through the quartz window from the mercury-in-quartz

arc which was fed by a current of 1.85 amperes. The arc was placed about 20 cm. from the disk to be illuminated. By means of diaphragms with circular openings of various sizes it was arranged that the *whole* surface of the disk was acted upon by the light. (It is essential that the whole surface be illuminated, for if the light modifies the surface, the face of the disk remains no longer homogeneous. It is not possible to determine the exact change effected in the contact potential by the

TABLE II.

Metal.	Contact P.D.'s Before Illumination.	Contact P.D.'s After Illumination for 10 Min.	2 Hrs. Later.	6 Hrs.	20 Hrs.	30 Hrs.	42 Hrs.
Silver	−.087	−.082	−.078	−.084	−.084	−.087	−.085
Tin	+.225	+.326	+.318	+.306	+.263	+.240	+.229
Magnesium	+.87	+.79	+.84	+.85	+.87	+.85	+.86
Zinc	+.244	+.352	+.347	+.325	+.288	+.252	+.238
Aluminum	+.367	+.333	+.350	+.355	+.362	+.373	+.370
Iron	+.033	+.075	+.072	+.067	+.064	+.056	+.053
Copper	−.070	−.166	−.125	−.117	−.097	−.096	−.096
Brass	−.034	−.137	−.083	−.070	−.047	−.044	−.041

light unless it be known just what fraction of the surface was illuminated. The contact potential of such a composite surface would be the average of the modified and unmodified portions of the surface.) Tables II. and III. show not only the manner in which contact potentials of film-

TABLE III.

Metal.	Contact P.D.'s Before Illumination.	Contact P.D.'s After Illumination for 2 Hours.	4 Hrs. later.	10 Hrs.	1 Day.	2 Days.	3 Days.	8 Days.
Silver	−.086	−.076	−.077	−.080	−.077	−.083	−.080	−.095
Tin	+.225	+.357	+.345	+.276	+.263	+.244	+.242	+.254
Magnesium	+.87	+.57	+.67	+.74	+.79	+.81	+.83	+.848
Zinc	+.264	+.540	+.452	+.362	+.293	+.287	+.287	+.237
Aluminum	+.362	+.193	+.286	+.333	+.346	+.353	+.343	+.372
Iron	+.042	+.093	+.090	+.087	+.084	+.080	+.087	+.082
Copper	−.083	−.195	−.142	−.113	−.105	−.096	−.095	−.100
Brass	−.045	−.190	−.111	−.088	−.080	−.063	−.072	−.072

coated surfaces are modified under the influence of ultra-violet light but also the manner in which the metals recover from the effect.

Several similar series of measurements were made and in all cases magnesium, aluminum, copper, and brass became more electro-negative,

while silver, tin, zinc, and iron became more electro-positive under the action of the light. With prolonged illumination the changes brought about in the contact potentials are greater and the recovery of the metals is in general less rapid and less complete than when the surfaces are exposed for but a short time, for it is seen that with ten minutes' exposure, Table II., to ultra-violet light, the recovery is on the whole more complete than with two hours' exposure, Table III., indicating that in the latter case the surfaces have been more or less permanently modified. By using much intenser illumination than that used in these cases, it was possible to produce even greater changes. Thus, zinc and magnesium, the one becoming more electro-positive and the other more electro-negative, could be made to change their order in the contact potential series.

There is no doubt that film coated surfaces are modified by ultra-violet light, but the fact that both positive and negative effects may be produced finds no ready explanation. If all the surfaces had become more electro-positive it might be supposed that they had been to a certain extent freed from gas or oxide films. On the other hand if all had become more electro-negative, it might be supposed either that a film or some modification equivalent to one had formed or that electrons freed from the metal had imbedded themselves in a film already existing. It is probable that something of the nature of both of these possibilities exists and what is observed is a resultant effect which depends upon the individual characteristics of the film and the metal. In any case it is almost certain that the surface becomes a non-homogeneous one, if not indeed already such, so that the measurements give merely the average effect of the constituents of the composite surface.

THE RELATION BETWEEN CONTACT AND PHOTO-POTENTIALS WITH FILM-COATED SURFACES.

Compton has shown[1] that the contact potentials of photo-electrically excited metals must be considered in conjunction with the applied accelerating potentials in measurements on photo-currents. By using different receiving electrodes he found that the distribution of velocity curves were all of practically the same shape but merely separated with reference to each other along the voltage axis by amounts equal to the contact differences of potential between the electrodes. Richardson and Compton[2] using analyzed light, found that for all wave-lengths and for all the metals, the maximum currents were reached when the potential

[1] Phil. Mag., 23, pp. 579–593, Apr., 1912.
[2] Phil. Mag., 24, pp. 575–594.

difference between the excited plate and the receiving electrode was zero volts, proper account of course being taken of the contact potential differences. These contact potential differences were not measured under the conditions which obtained when the metals were under examination but were assumed to be the same as those for undisturbed surfaces in air. This assumption may not always be correct, although it seems to have been so in their experiments. Their point of view, however, in regard to the manner in which contact potential differences are to be taken into account is supported by this work.

TABLE IV.

Metal.	Contact P.D.'s Against Brass Plate.	Accelerating P.D.'s for ¾ Saturation.	Contact P.D.'s with Copper.	Differences in Accelerating P.D.'s.
Silver	−.08	−.25	+.11	+.07
Magnesium	+.53	−.89	+.72	+.71
Zinc	+.49	−.91	+.68	+.73
Aluminum	+.23	−.53	+.42	+.35
Tin	+.28	−.69	+.47	+.51
Iron	+.09	−.45	+.28	+.27
Brass	−.18	−.16	+.01	−.02
Copper	−.19	−.18	00	00

Owing to the fact that film coated surfaces suffer changes when excited, it was difficult to duplicate distribution of velocity curves or to determine accurately the point at which the saturation current is reached. Therefore, instead of plotting the complete curve or locating the point at which saturation occurs, merely the saturation current was found and then such a potential was applied to the excited plate that the current was reduced to three fourths of the saturation value. This was indeed an arbitrary proceeding but nevertheless one giving reliable and definite information in regard to the general way in which the contact potentials and accelerating potentials are related. Table IV. gives a sample series of results obtained when the plates had been previously strongly illuminated in order to bring them into a modified condition which could be approximately maintained. The last two columns indicate a fair agreement between the differences in the contact potential differences and those in the accelerating potentials. Exact agreement is not to be expected for the applied potential necessary to produce the saturation current from a given metal is a variable quantity depending on the condition of the surface. In fact the complete velocity curve may be greatly altered in its general shape and inclination as well as shifted bodily along the voltage axis by changes in the surface.

The apparent initial velocities of emission of the electrons from illuminated surfaces are thus also dependent upon surface conditions. Nor is this dependence such as always to make the modifications in the contact potentials responsible for some of the changes observed to take place. Thus in the case of magnesium, which was found to become more electro-negative with illumination, the initial velocities of emission became greater just as though the surface had become more electro-positive rather than more electro-negative. In seeking an explanation of this fact, it may be supposed that the film covering the surface is, if not neutral, neither strongly positive nor negative, and in parts at least not of sufficient thickness to screen off the intrinsic contact effects of the metal itself. Then it is possible also to conceive of this film as being broken up by illumination in such a way as either to present more relatively inactive surface or to increase its screening effect while at the same time the broken film allows the electrons to escape more readily than before. Such an explanation is strengthened by the additional fact that the magnesium surface after a considerable period of rest, thus permitting the formation of a film, would become increasingly photo-sensitive with a somewhat prolonged exposure to ultra-violet light.

CONTACT POTENTIALS WITH NEWLY PREPARED SURFACES IN VACUO.

The only way to prepare a pure and approximately film-free surface of any of the ordinary metals is to cut away the metal. If this is done in a good vacuum, the best possible conditions have been established for the study of the properties of clean metallic surfaces. It was for this reason that provision was made to scrape off the old surfaces in

TABLE V.

Metal.	Contact P.D's Before Scraping.	Contact P.D's After Scraping.	24 Hrs. Later.	2 Days.	4 Days.
Aluminum.....	+.293	+1.04	+.94	+.895	+.874
Iron.....	+.053	+ .24	+.217	+.205	+.192
Copper.....	−.106	+ .10	+.060	−.068	−.110
Silver.....	−.097	+ .05	+.021	−.003	.000
Tin.....	+.216	+ .32	+.330	+.324	+.317
Magnesium.....	+.825	+1.47	+.81	+.724	+.713
Zinc.....	+.193	+ .64	+.56	+.512	+.496
Brass.....	−.123	+ .26	+.243	+.227	+.228

vacuo. As soon after the scraping was done as adjustments could be conveniently made, the contact potentials against the movable brass plate were measured. The best obtainable vacuum was maintained

throughout. In Table V. the first column gives the values observed just before, and the second column those just after, polishing. The metals are all more electro-positive as a result of polishing, just as would have been the case had the operations taken place in air. As the last three columns show, the metals tend to become more electro-negative with time, the rate of change being relatively quite different for the different metals. It is interesting to note that after four days copper and magnesium have become more electro-negative than they had been at any time previous to the scraping except when recently subjected to the action of the ultra-violet light.

TABLE VI.

Metal.	Contact P.D.'s Before Illumination.	Contact P.D.'s After Illumination.
Silver	+.010	+.014
Magnesium	+.753	+.760
Zinc	+.513	+.498
Aluminum	+.953	+.961
Tin	+.305	+.312
Iron	+.189	+.200
Brass	+.222	+.215
Copper	−.068	−.077

Agreement has not yet been reached in regard to a theory of the true nature of the phenomenon. These results, however, do not strengthen an electrolytic theory, but tend rather to support the view that the pure metals exhibit definite and characteristic potentials because of intrinsic properties which manifest themselves in this manner at the surface. Chemical action is to be considered not so much because of itself as because of the products resulting from it. When a metallic surface has become oxidized or is covered with any sort of a film, the effect observed is essentially that of a composite surface, both film and metal contributing to the general effect except when the film is of such thickness or so disposed as to screen off entirely the effects of the metal.

This point of view is further supported by the fact that with clean surfaces in vacuo, exposure to ultra-violet light produces a little or no change in the contact potentials. Table VI. gives the values obtained before and after 15 minutes' illumination with surfaces which had been prepared about 24 hours previously. It was decided to examine them at this stage in order that the ageing effect which proceeds more rapidly shortly after the scraping of the surface has taken place than it does later, would not mask such changes as might be produced by the action of the light. The changes observed are not great enough to make it

possible to assert positively that they are brought about by the illumination. Even if they are due wholly to the action of the light, they are so small relatively that, for the short intervals of illumination which usually obtain in photo-electric studies, it may be safely assumed that no appreciable changes in the contact potentials of surfaces recently prepared in vacuo take place as a result of exposure to the light. It is certain, however, that even with surfaces prepared in vacuo, the presence of films is not completely eliminated. They must begin to form as soon as polishing ceases but it may be taken for granted that they are very much thinner and cover more imperfectly the metals underneath than the old films which were removed. The metals are therefore exposed more directly to the light and hence the results in Table VI. show that the metals themselves are not modified so far as their contact potentials are concerned. On the other hand, since with old films great differences are produced it is more than probable that all the changes which are observed in contact potentials as a result of photo-electric treatment are due to modifications brought about in these films.

PHOTO-CURRENTS FROM SURFACES RECENTLY PREPARED IN VACUO.

The distribution of velocity curves with surfaces recently prepared in vacuo were plotted and are shown in Figs. 3 to 8. They are arranged in pairs and some are repeated in order to show more clearly the relations

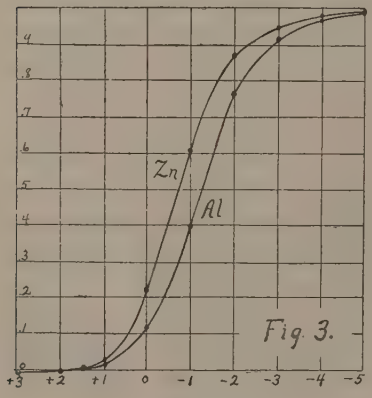

Fig. 3.

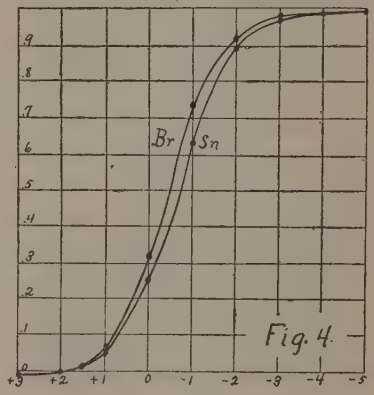

Fig. 4.

existing between them. All have not been shown in a single figure in order to avoid confusion. When −8 volts were applied to the illuminated disk, the photo-current was approximately a maximum in all cases. In plotting the curves this current is taken as unity. There is a slight

effect due to reflected light as indicated by the fact that the velocity curves cross the axis of zero current. This makes it impossible to determine the true positive potentials acquired by the metals when illuminated with unanalyzed ultra-violet light. It is interesting to note, however, that except in the case of magnesium, the point at which the axis is crossed by these curves is approximately the same for all the metals, lying between +1.7 and +1.9 volts. The true positive potential is undoubtedly somewhat greater and it would seem that with perfectly clean surfaces it is the same for all the metals. If this is the actual state of affairs, the more electro-positive a metal is, the greater is the retarding potential, taking into account of course the contact potential of the metal,

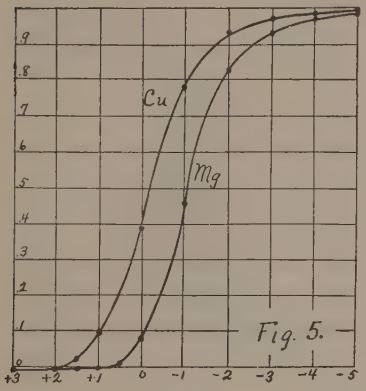

Fig. 5.

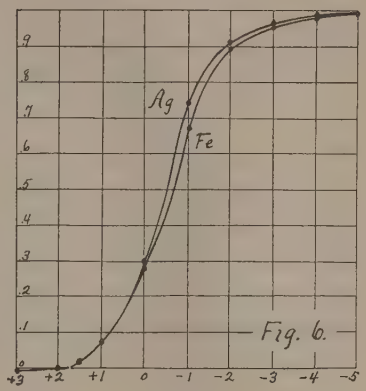

Fig. 6.

necessary to keep the electrons from escaping. For magnesium this point, in the case of the curve plotted, corresponds to about +.7 volt. This does not mean that magnesium differs fundamentally from the other metals. It must be mentioned that these curves were not plotted until a few hours after scraping for the reason that the photo-sensitiveness of newly formed surfaces decreases very rapidly with time. This is particularly true of magnesium. It was necessary, therefore, that the surface be old enough that its photo-sensitiveness remain practically unchanged during the interval necessary to make the observations for a complete curve. Consequently the surfaces cannot be considered absolutely free from films, for these are sure to form even in the best obtainable vacuum. The magnesium surface, as would be expected from the readiness with which it oxidizes, merely shows in a more striking manner any modification that may be taking place. With magnesium surfaces newer than the one for which the curves are shown, the current

axis is crossed at points farther to the left, *i. e.*, the more or less common point for the other metals is approached nearer and nearer the newer the magnesium surface. With older surfaces this point shifts to the right and in fact, with the previously undisturbed surface, the current axis was crossed at $-.3$ volt. The same effect may be observed with the other metals, but it is so small as to be practically negligible. Hence it may be stated as a general fact that the apparent initial velocity of emission of electrons is less for old, than it is for new, surfaces in spite of the fact that the new surfaces are more electro-positive than the old. The effect is due in part to the electrons liberated from the receiving electrode by light of the higher frequencies reflected from the illuminated

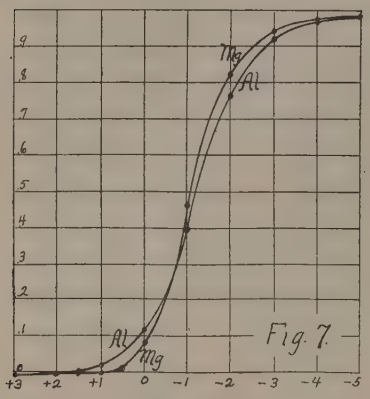

Fig. 7.

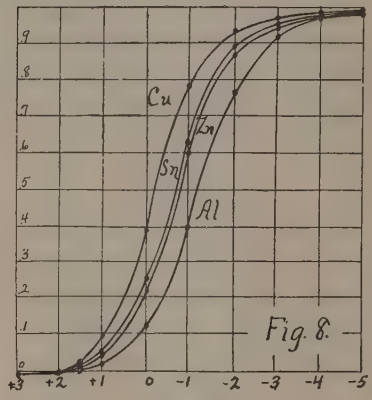

Fig. 8.

surface. This is because the old surfaces are less photo-sensitive than the new, while the number of electrons due to reflected light is practically the same for both and hence the point at which the axis of zero current is crossed by the distribution of velocity curves is further to the right with old than with new surfaces. It seems certain, however, that the film acts also as a mechanical barrier to the passage of electrons from the metal, for the shift of the curve, in the case of magnesium at least, is greater than can be accounted for by the action of electrons liberated from the receiving electrode.

Pushing further the comparison of the magnesium curve with those of the other metals, it will be seen from Fig. 7 that the magnesium curve rises more abruptly than the aluminum curve, crosses the latter and again meets it by turning more abruptly upon approaching the maximum. As stated before, this was a surface a few hours old. With a newer surface, the curve may be wholly to the right of, and approach

more nearly the same general shape as, that for aluminum. On the other hand, with an older aluminum surface the curve approaches the general shape of that for magnesium here shown. These facts also indicate that the film must be considered as a sort of barrier to the passage of electrons from the metal and as exhibiting a contact potential and photo-electric properties of its own which are superimposed upon, or screen off in part, those of the metal beneath.

TABLE VII.

Metal.	Contact P. D.'s.	Apparent Positive Potentials.
Silver	+.024	1.92
Magnesium	+.782	.82
Zinc	+.543	1.75
Aluminum	+.967	1.83
Tin	+.320	1.74
Iron	+.225	1.90
Brass	+.222	1.75
Copper	−.042	1.87

Table VII. gives in the first column the contact potentials of the several metal surfaces against the movable brass plate when the observations for these curves were made. The second column gives the values of the apparent positive potentials acquired by the metals when the disk to be examined was placed in communication with the electrometer and when the wire gauze cylinder previously used as receiving electrode was earthed. These apparent positive potentials are in fair agreement with those indicated by the curves in Figs. 3–8.

Considering all the curves together, it is seen that they tend to emerge from a more or less common point spreading out fan-like at first and later assuming approximately the same general shape, and that the order thus assumed by the metals is that of their contact potentials. The latter fact furnishes substantial evidence that the differences in the applied potentials necessary to produce the saturation current coincide in a general way with those in the observed contact potential differences. That this should be so is more readily explained by assuming that inherent physical properties of the metals rather than chemical action are coming into play.

THE RELATIVE PHOTO-SENSITIVENESS OF METALLIC SURFACES.

It has been stated that the photo-sensitiveness of the newly prepared metallic surfaces is greater than it is for older surfaces. Observations on the photo-sensitiveness of the metals were made both before and

after scraping in order to determine, not only the difference in sensitiveness of new and old surfaces but also the relative sensitiveness of the series of metals, with a view to ascertain if it be related to the contact series. The first column of results in Table VIII. gives the relative photo-sensitiveness of the old unscraped surfaces. It is seen that silver was the most and magnesium the least sensitive of the eight metals, and that the order is not at all that of their contact potentials. (See first column, Table II. or III., for contact potential differences of the old undisturbed surfaces.) In the second and fourth columns of Table VIII. are given two series of results showing the relative sensitiveness of comparatively new surfaces, two days and one day respectively after scraping, and the third and fifth columns give the relative sensitiveness of the metal surfaces just as soon after scraping as observations could be made.

TABLE VIII.

Metal.	Relative Photosensitiveness.				
	Old Original Surfaces.	New Surfaces.			
		I.		II.	
		Before Scraping.	After Scraping.	Before Scraping.	After Scraping.
Silver	28	34	51	32	45
Magnesium	4	28	1000	42	1000
Zinc	5	49	78	53	87
Aluminum	7	190	*470	260	560
Tin	19	42	69	45	72
Iron	10	38	65	46	67
Brass	17	34	46	30	45
Copper	13	40	62	40	58

(See second column, Table V.—contact potential differences of the metals just after scraping, and the third and fourth columns, those one day and two days later.) With the newly scraped surfaces magnesium is by far the most photo-sensitive just as it is the most electro-positive. Its photo-sensitiveness is taken as the base for comparison and is for convenience given a value of 1,000. With the newly scraped surfaces the order of the metals, with the single exception of brass, is seen to be exactly that of the contact series. Any given order does not long persist, however, because the aging of the various surfaces proceeds at relatively widely different rates. Thus magnesium, which is at the head of the list directly after scraping, finds its place at the bottom in two days.

It is known that the highly electro-positive metals, sodium and potassium, are exceedingly sensitive to light. There is not wanting evi-

dence, therefore, that the photo-sensitiveness of clean metallic surfaces is related to their contact potentials.

CONCLUSIONS.

The point of view that the so-called contact potentials are due to intrinsic properties of the metals finds substantial support on the basis of the results of this investigation. The considerations leading to this conclusion may be briefly stated as follows:

1. The metals become more electro-positive when new surfaces are prepared in the best obtainable vacuum.

2. The changes in contact potential differences which are observed to take place in film-coated surfaces subjected to photo-electric treatment are such as to indicate that whatever the modifications are, they take place in the film and not in the metal.

3. The observed initial velocities of emission of electrons from recently prepared surfaces are nearly the same for all metals, suggesting that the more electro-positive a metal is, the greater the actual velocity of emission of electrons from its surface.

4. The apparent initial velocities of electrons are less for film coated than for clean surfaces and not in a manner to be accounted for by accompanying changes observed in the contact potentials. To the extent that this is not explained by the differences between the relative effects of the direct illumination and the electrons set free by reflected light for the new and old surfaces, the film acts as a mere mechanical obstruction in addition to serving as an electric screen or contributing to the electrical field.

5. The fact that the differences in the applied accelerating potentials necessary to produce the saturation currents from clean metallic surfaces under illumination coincide in a general way with those in the observed contact potential differences would not be cited as evidence in favor of an electrolytic or chemical theory of contact potentials.

6. Since the photo-sensitiveness of the metals is much greater with new than with old surfaces, and since the order assumed by metals with clean surfaces is practically that of the contact series, it appears that the electro-positive character of a pure metal is an index of the readiness with which it gives up electrons.

A comprehensive view of the above considerations shows that the facts not only warrant the suggestion that the contact potentials are manifestations of inherent properties of the metals, but also throw some light on what the nature of these properties may be. None of the facts are contradicted by supposing that the electro-positive or electro-negative

character of the metal has to do with its ability to retain electrons or its tendency to discharge them. This is essentially the view held by Helmholtz, who conceived of the metals as having specific attractions for positive and negative electricities, the nature and intensity of the electrification displayed by a given metal representing the difference between its attractions for the two kinds.

I take this opportunity to thank Professor Millikan for his counsel and encouragement at all stages of this research and to acknowledge my indebtedness to Mr. Julius Pearson, the mechanician at the Ryerson Physical Laboratory, whose ingenuity and skill made it possible for me to realize and to put into successful operation the apparatus designed for this work.

RYERSON LABORATORY,
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